Initial Stages of Growth of Copper on MgO(100): A First Principles Study

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We have studied the energetical and structural properties of copper clusters (Cu_n, $n = 2$–6, 8, 9, 13, 14, 25, and 29) and films (with $n_L = 1$, 2, and 3 layers) adsorbed on MgO(100) by means of first principles density functional calculations. We find that Cu-Cu interactions dominate over Cu-surface interactions, so that three dimensional (3D) structures are largely preferred with respect to two dimensional (2D) ones. This indicates a Volmer-Weber growth mode for Cu on MgO(100), in agreement with recent experimental observations.

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Metal/oxide interfaces have an important role in many technological applications, ranging from heterogeneous catalysis to microelectronics. This has motivated an increasing interest towards the fundamental physical and chemical properties of these systems over the last years [1]. In particular, many experiments have examined the initial stages of formation of the metal/oxide interface, and addressed questions such as the character and the strength of the bonding between the metal atoms and the oxide substrate, the growth mode and the morphology of the growing film, and the mechanisms of strain relaxation in the film. Theoretical studies, on the other hand, have mostly focused on the adsorption of either a single metal adatom or of a thin uniform film, and have not considered issues more related to the growth properties, e.g., what are the preferred structures of adsorbed metallic aggregates, how the metal-surface interaction varies with the particle size, etc.

Owing to its stability up to very high temperatures, one of the substrates which is more frequently used in experimental investigations is the (100) surface of magnesium oxide. In this work, we examine the growth properties of a representative metal, copper, on MgO(100), by means of density functional calculations in which adsorbed copper clusters and films of different size (Cu_n, $n = 2$–6, 8, 9, 13, 14, 25, and 29) and thickness ($n_L = 1$, 2, and 3 layers) are considered. Cu/MgO(100) is a system characterized by a large mismatch between the Cu and MgO lattice constants, $f = (a_{\mathrm{MgO}} - a_{\mathrm{Cu}})/a_{\mathrm{MgO}} \sim 15\%$. Moreover, since the Cu surface energy, $\sim 1.9\ \mathrm{J\,m^{-2}}$, is larger than that, $\sim 1.1\ \mathrm{J\,m^{-2}}$, of MgO(100), thermodynamics predicts a Volmer-Weber (VW) growth, i.e., 3D Cu clusters should form on top of the MgO(100) substrate [2]. Instead, experimental studies have yielded conflicting results. Moeller and co-workers [3] found that Cu films grow in (100) orientation on the MgO(100) substrate, and that the growth follows the Stranski-Krastanov (SK) mode (one complete monolayer followed by three dimensional islands). Conard *et al.* [4] confirmed the SK growth mode, but further claimed that the first complete layer was a $\mathrm{Cu_2O}$ layer rather than metallic Cu. More recently, however, Zhou *et al.* [5] reported that the growth is VW, and attributed the earlier observations of SK growth to the fact that MgO(100) surfaces containing high concentrations of defects had been used.

The results of this work confirm the thermodynamical arguments as well as the conclusions of Zhou *et al.* In fact, we find that on a *defect-free* surface, copper adatoms largely prefer to bind to other Cu atoms rather than to MgO surface atoms. The strength of the Cu-Cu bond, together with the large lattice mismatch between Cu and MgO, effectively prevents the wetting of the surface and thus the formation of a uniform overlayer. Deposited metal atoms preferentially form 3D aggregates over the MgO substrate thus following the VW mode of growth.

Calculations have been carried out using a plane-wave-pseudopotential approach within the local density approximation (LDA), and including gradient corrections non-self-consistently within the generalized gradient approximation (GGA) [6]. This "post-LDA" approximation (hereafter denoted pGGA) has been found to work very well in recent work on Cu surfaces [7] and clusters [8]. In addition, we explicitly verified that pGGA and fully self-consistent GGA binding energies agree closely for all adsorbed Cu_n clusters with $n = 1$–4 [9]. To model the MgO(100) surface, a slab of only two atomic layers was found sufficient, since practically identical adsorption energies and bond distances were obtained for a single Cu adatom and a $\mathrm{Cu_5}$ cluster when the slab thickness was increased from two to three layers (clusters or films are adsorbed on one side of the slab) [10]. For the study of the adsorbed clusters, supercells containing 18, 36, and 50 atoms per layer were employed, depending on the cluster size. The same cells were used for the corresponding *free* clusters (see below). For these calculations, k sampling was restricted to the Γ point. Tests on free and adsorbed $\mathrm{Cu_5}$ clusters show binding energy differences of ~ 0.03 eV per Cu atom when the supercell size is increased from 18 to 36 atoms/layer. Calculations for the adsorbed films were performed using the primitive surface cell, and in that case, 10 **k** points in the irreducible part of the corresponding Brillouin zone, with a Gaussian smearing of width 0.05 Ry, were used [11]. Other details and tests on the accuracy of the calculations are reported in Refs. [9,14]. In several cases, the thermal stability of the calculated structures was checked by means of first principles molecular dynamics simulations [12].

To study the adsorbed clusters, for each cluster size n, one or more "likely" initial geometries were selected and fully optimized. These initial structures were chosen by taking into account that, in the absence of defects, Cu preferably binds to O sites of the surface [14–17]. For Cu_n adsorbed clusters with $n = 2$–5, an extensive search of the most stable adsorption configurations was carried out. We find that these are similar to the lowest energy structures in the gas phase [8,18], with the cluster in an upright position over the surface: for Cu_2, the preferred adsorption geometry has a tilt angle of $\sim 5°$ with respect to the surface normal; for $n = 3$–5, the most stable conformations are standing triangle, rhombus, and trapezoid, respectively [19]. For $n = 6, 8$ only a few configurations have been studied. Upon relaxation, geometries initially 2D tend to transform into 3D structures having the character of fcc fragments. Thus, for $n \geq 9$, we have examined a few (small) fcc islands having the shape of pyramids or truncated pyramids, as frequently observed in the growth of metals on oxide surfaces [1] (see Fig. 1). For Cu_9 we started from a monolayer 3×3 square island. Upon relaxation, the island did not stay flat, but evolved towards a weakly 3D fourfold star geometry. Cu_{13} (Cu_{14}) is a two-layer (three-layer) fcc truncated pyramid (pyramid) made up of a base of nine atoms and a second layer of four atoms. Finally, Cu_{25} and Cu_{29} are two- and three-layer fcc islands (truncated pyramids), both having a base of 16 ($= 4 \times 4$) atoms. The structure of Cu_{29} shows the presence of a core where Cu-Cu distances tend to match the O-O separation in the substrate, while shorter Cu-Cu distances (~ 2.5 Å) are present near the corners and in the upper layers (see Fig. 1).

To analyze the energetics of the adsorbed clusters, we compare the adsorbate-adsorbate intracluster cohesion $E_{A\text{-}A}$, to the surface-adsorbate binding, $E_{S\text{-}A}$. For a cluster of n Cu atoms, we define $E_{S\text{-}A}$ as

$$E_{S\text{-}A}(n) = -[E^{\mathrm{ads}}_{\mathrm{Cu}_n} - E_{\mathrm{slab}} - E^{\mathrm{free}}_{\mathrm{Cu}_n}]/n\,, \tag{1}$$

where $E^{\mathrm{ads}}_{\mathrm{Cu}_n}$ is the total energy of the adsorbate-substrate system, E_{slab} is the energy of the clean surface, and $E^{\mathrm{free}}_{\mathrm{Cu}_n}$ is the energy of the free cluster [20]. Similarly, we define the intracluster binding energy $E_{A\text{-}A}$, which is the energy required to dissociate the cluster into n noninteracting Cu adatoms, as

$$E_{A\text{-}A}(n) = -[E^{\mathrm{ads}}_{\mathrm{Cu}_n} + (n - 1)E_{\mathrm{slab}} - nE^{\mathrm{ads}}_{\mathrm{Cu}_1}]/n\,, \tag{2}$$

where $E^{\mathrm{ads}}_{\mathrm{Cu}_1}$ is the total energy for the surface with a single adsorbed adatom. In Fig. 2, our results for $E_{S\text{-}A}$ and $E_{A\text{-}A}$ are summarized. With increasing n, the adsorption energy per atom $E_{S\text{-}A}$ decreases, while $E_{A\text{-}A}$ increases. The dips in $E_{A\text{-}A}$ for $n = 6$ and $n = 9$ reflect the fact that the structures we examined are not energetically favored, while the peaks in both $E_{S\text{-}A}$ and $E_{A\text{-}A}$ suggest that these adsorbed clusters are particularly stable. Figure 2 clearly shows that Cu adatoms prefer to bind to other Cu adatoms than to oxygen surface atoms: for $n > 2$, the Cu-Cu cohesion forces dominate and the subsequent energetically preferred structures are all upright or three dimensional [21].

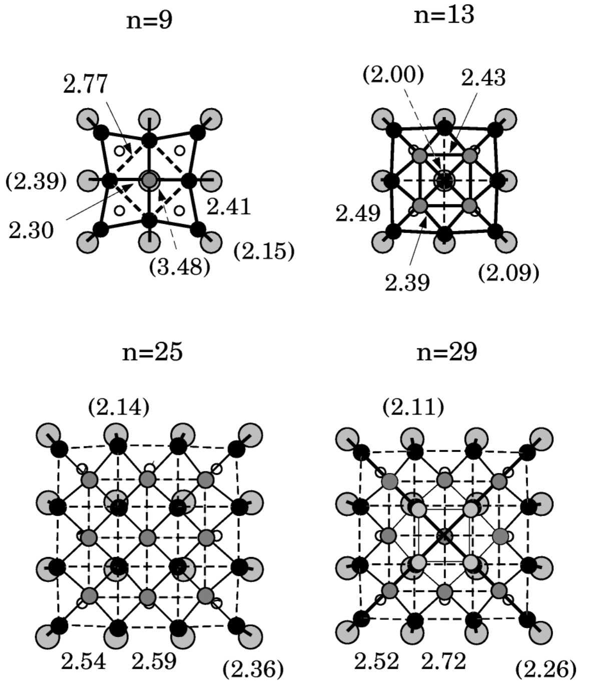

FIG. 1. Relaxed structures (top views) for Cu_9, Cu_{13}, Cu_{25}, and Cu_{29} on MgO(100). Large grey (small empty) circles represent oxygen (magnesium) surface atoms. Small filled black, dark grey, and light grey circles represent first, second, and third layer copper adatoms, respectively. Bond lengths are in Å. Numbers in parentheses denote Cu-O distances.

Evidence for the similarity of free and adsorbed Cu clusters is provided by Fig. 3, where we compare the cohesive energies per atom,

$$E_{\mathrm{coh}}(n) = -[E^{\mathrm{ads}}_{\mathrm{Cu}_n} - E_{\mathrm{slab}} - nE^{\mathrm{free}}_{\mathrm{Cu}_1}]/n\,, \tag{3}$$

and structural parameters of free and adsorbed clusters, respectively. We can see that $E_{\mathrm{coh}}(n)$ is typically a few tenths of an eV higher than that of the free clusters. The only exception is Cu_{25}, for which the free cluster undergoes an important rearrangement with respect to the adsorbed structure, which significantly lowers its energy. Figure 3 also shows that copper clusters adsorb on the surface with increasing $d_{S\text{-}A}$ and $d_{A\text{-}A}$ distances when n increases, with asymptotic values of ~ 2.1 and 2.4 Å, respectively. The clusters do not drastically modify their gas-phase interatomic distances to satisfy surface bonding, as shown by the close similarity of $d_{A\text{-}A}$ values for the adsorbed and free clusters.

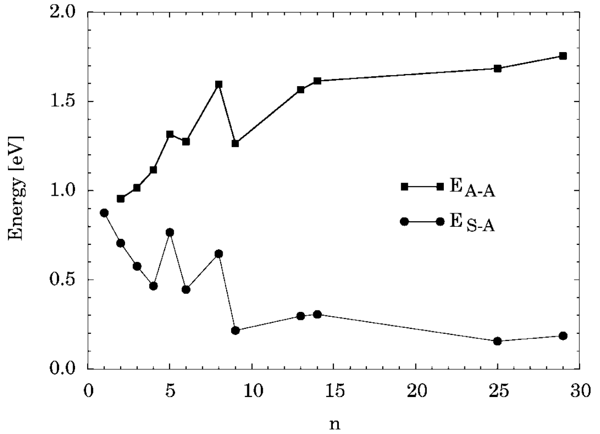

FIG. 2. Binding energies for copper clusters on MgO(100). $E_{S\text{-}A}$ and $E_{A\text{-}A}$ are defined in Eqs. (1) and (2), respectively.

The results in Figs. 2 and 3 clearly support a VW mode of growth for Cu on MgO(100), at variance with early observations of SK growth [3,4]. To further investigate the possible occurrence of Cu wetting layers, we consider uniform strained films (with $n_L = 1, 2,$ and 3 layers), in which the Cu atoms of the first layer sit on top of the surface oxygens of the substrate, while successive layers follow an fcc stacking. In Table I, the cohesive energies per Cu atom in the adsorbed film, $\epsilon_{\mathrm{ads}}^{(L)}$, are compared to the corresponding energies, $\epsilon_{\mathrm{free}}^{(L)}$, of "free" Cu films in the vacuum. Also reported are the cohesive energies per atom for bulk Cu, in the equilibrium fcc structure, and in a tetragonal structure which has the same in-plane lattice parameter of the epitaxial film, and c/a obtained via optimization.

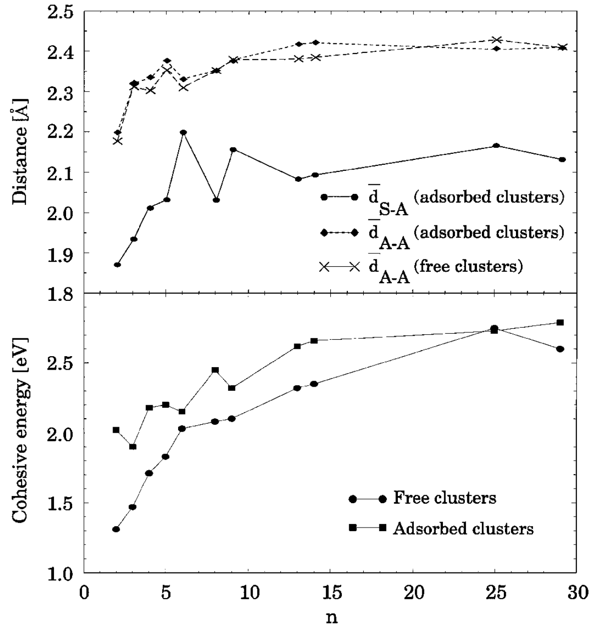

FIG. 3. Lower panel: comparison between the cohesive energies per atom of free and adsorbed clusters. Upper panel: average $d_{S\text{-}A}$ and $d_{A\text{-}A}$ distances (LDA) for relaxed Cu$_n$ ($n = 2$–6, 8, 9, 13, 14, 25, and 29) clusters, in both their gas phase and adsorbed geometries.

TABLE I. Cohesive energies per atom (eV) for pseudomorphic Cu films on MgO(100) and free Cu films in the vacuum. For the free films, the theoretical equilibrium lattice constant of bulk Cu (3.55 Å) is used as the in-plane lattice constant. The entries $n_L = \infty$ correspond to strained tetragonal and fcc Cu bulk, respectively.

n_L	$\epsilon_{\mathrm{ads}}^{(L)}$	$\epsilon_{\mathrm{free}}^{(L)}$
1	2.08	2.42
2	2.92	2.93
3	3.07	3.12
∞	3.46	3.49

The close similarity of the energies for these structures is a remarkable feature which has been recently discussed in the literature [23]. Table I shows that $\epsilon_{\mathrm{ads}}^{(L)}$ is always smaller than the cohesion energy for the bulk. This confirms that under conditions of thermodynamic equilibrium the growth should follow the VW mode, since large bulk-like 3D clusters are energetically preferred to the coherently strained layers [2]. For each n_L, and especially for $n_L = 1$, $\epsilon_{\mathrm{free}}^{(L)}$ is slightly larger than the corresponding $\epsilon_{\mathrm{ads}}^{(L)}$. By identifying the "free Cu films" with incommensurate overlayers having an extremely weak adhesion with the MgO substrate, one may infer that the adsorbed pseudomorphic films would gain energy by losing their adhesion and becoming incommensurate with the substrate. Most likely, however, other mechanisms of strain relaxation should lead to a greater energy gain (see below).

We now compare the energy of a Cu atom in an island with that in a uniform strained film, by expressing the total cohesion energy $\mathcal{E}_{\mathrm{coh}}^{(L)}(n)$ for an adsorbed island of n atoms and L layers in the form $\mathcal{E}_{\mathrm{coh}}^{(L)}(n) = \epsilon_{\mathrm{ads}}^{(L)}\, n +$ corrections, where the corrections to $\epsilon_{\mathrm{ads}}^{(L)}$ take care of the fact that the island is finite, i.e., it contains perimeter and corner atoms. When n is large enough, perimeter atoms contribute a term to $\mathcal{E}_{\mathrm{coh}}^{(L)}$ that is proportional to $\sqrt{n}$, while corner atoms contribute a term independent of n. Thus, the cohesive energy per atom becomes

$$E_{\mathrm{coh}}^{(L)}(n) = \epsilon_{\mathrm{ads}}^{(L)} - \epsilon_{p}^{(L)} \frac{1}{\sqrt{n}} - \epsilon_{c}^{(L)} \frac{1}{n}, \qquad (4)$$

where $\epsilon_p^{(L)}$ ($\epsilon_c^{(L)}$) is the excess energy due to edge (corner) atoms in the island. Cohesive energies $E_{\mathrm{coh}}^{(L)}(n)$ for two- and three-layers islands ($L = 2, 3$), and for the smaller ($n \leq 8$) clusters, are represented in Fig. 4, together with the results for the uniform monolayer, bilayer, and trilayer Cu films and the Cu bulk. For $L = 2$, the curve which interpolates the infinite bilayer, $n = 13$ and $n = 25$ energies has $\epsilon_{\mathrm{ads}}^{(2)}$, $\epsilon_p^{(2)}$ and $\epsilon_c^{(2)}$ equal to 2.92, 0.60, and 1.73 eV, respectively, while for $L = 3$ data points from the infinite trilayer, $n = 14$ and $n = 29$ can be interpolated by a straight line with $\epsilon_{\mathrm{ads}}^{(3)} = 3.07$ eV and $\epsilon_p^{(3)} = 1.53$ eV.

From Fig. 4, we can see that the cohesive energies for all small ($n \leq 8$) clusters fall at or below the two

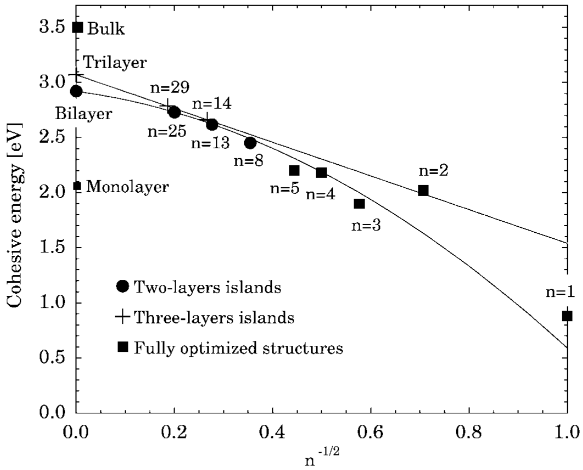

FIG. 4. Cohesive energy per atom for various adsorbed Cu structures on MgO(100). Symbols are calculated values; the curve and the straight line have been interpolated as described in the text.

interpolated curves for two- and three-layer islands. Vice versa, the cohesive energy for the strained monolayer film is smaller than the energy of all adsorbed clusters with $n \geq 4$, implying that this film is unstable towards the formation of rather small clusters. Similarly, for the case of a uniform bilayer [24], by comparing $\epsilon_{\mathrm{ads}}^{(2)}$ to $E_{\mathrm{coh}}^{(3)}(n)$ we find that the film is unstable towards the formation of three-layer islands containing more than ~104 Cu atoms. This analysis—extended to include islands and films of four and more layers—provides the minimum size of islands against which uniform films are unstable [24]. It appears that this minimum size increases with increasing overlayer thickness. It is known, however, that for thick films and large islands the formation of misfit dislocations can provide an efficient mechanism of strain relaxation. A more complete analysis should therefore include the energetics of dislocated films and islands.

In conclusion, our results show that copper on MgO(100) grows according to the Volmer-Weber mode, thus supporting the recent suggestion [5] that earlier abbreviations of SK growth should be attributed to the presence of a large concentrations of defects. The main reason for the VW growth is that Cu adatoms prefer to bind to other Cu adatoms than to surface atoms, preventing the wetting of the surface by the deposited clusters and thus the formation of a stable overlayer.

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[20] $E_{\mathrm{Cu}_n}^{\mathrm{free}}$ is calculated by optimizing the structure of the cluster starting from the geometry of the adsorbed cluster on the surface. Thus, usually the resulting structure is not the one corresponding to the global minimum for the free Cu$_n$ cluster.
[21] Using the pGGA, the calculated adsorption energy for an isolated Cu adatom, $E_{S\text{-}A} = 0.88$ eV [14], while in broad agreement with experiment [22], is a few tenths of an eV larger than the value found using different exchange-correlation functionals [17]. However, the possibility that our calculations slightly overestimate the metal-surface interaction has little consequence on the main results of the present work, in which $E_{S\text{-}A}/E_{A\text{-}A} < 1$ for all $n \geq 2$.
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